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#### (54) Aqueous suspension concentrate

(57) The invention relates to an aqueous, concentrated suspension (SC) for crop protection active compounds which comprises

(a) 50 to 400 g/L of at least one crop protection active compound:

(b) 50 to 500 g/L of at least one adjuvant, which reduces the surface tension in the spray dilution 40 mN/m or less and does not promote the particle growth of the crop protection active compound; (c) at least one surfactant selected from the groups (c1) and (c2):

(c1) 5 to 75 g/L of one or more non-ionic dispersants,
(c2) 10 to 100 g/Lof one or more anionic disper-

(d) up to 150 g/L of one or more anti-freezing

(e) up to 25 g/Lof one or more defoamers, (f) up to 25 g/L of one or more preservatives, and (g) 200 to 800 g/L of water.

wherein the adjuvant (b) is selected from the group consisting of amine alkoxylates, polyoxyalkylene triglycerides, alkylpolyglycosides, alkenyl succinic anhydride derivatives, polyvinylpyrrolidones, perfluoroalkyl acids derivatives, and mixtures thereof;

and to the use of such a concentrate suspension as a pesticide.

#### Description

#### BACKGROUND OF THE INVENTION

5 [0001] This invention concerns an aqueous, storage stable suspension concentrate (SC) for crop protection active compounds, a method for the manufacture of such suspensions, and their use for combating pests.

[0002] As a rule inert ingredients must be used to bring crop protection active compounds, for example fungicidal compounds, into such a form that be user can apply them either as such or after diffusion with water. The correct choice of suitable inert ingredients for the formulation often determines to a significant extent whether the active ingredient can display its full efficacy after application. When selecting suitable ingredients to insure the physicochemical stability of the formulation, it must be taken into account that not every active ingredient can be processed into any given formulation tower without losses in stability and/or efficacy.

[0003] The efficacy of the active components can often be improved by addition of other ingredients such as adjuvants. An adjuvant is defined here as a substance which can increase the biological activity of an active ingredient but is not itself significantly biologically active. The adjuvant can either be included in the formulation or can be added to the spray lank together with the formulation containing the active ingredient.

[0004] In view of an easy and safe handling and dosing of these adjuvants by the end-user and in view of avoiding unnecessary packing material, it is desirable to develop concentrated formulations which already contain such adjuvants.

#### SUMMARY OF THE INVENTION

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[0005] The present invention relates to an aqueous, concentrated suspension (SC) for crop protection active compounds which comprises

- (a) 50 to 400 g/L of at least one crop protection active compound;
- (b) 50 to 500 g/L of at least one adjurant, which has the capability of reducing the surface tension in the spray dilution to 40 mN/m or lower and does not significantly promote the particle growth of the crop protection active compound in the stored SC;
- 30 (c) at least one surfactant selected from the groups (c1) and (c2):
  - (c1) 5 to 75 g/L of one or more non-ionic dispersants, and
  - (c2) 10 to 100 g/L of one or more anionic dispersants,
  - (d) up to 150 g/l of one or more anti-freezing agents,
  - (e) up to 25 g/L of one or more defoamers,
  - (f) up to 25 a/L of one or more preservative, and
  - (g) 200 to 800 g/L of water,
- wherein the adjuvant (b) is selected from the group consisting of amine alkoxylates, polyoxyalkylene triglycerides, alkyl-polyglycosides, alkenyl succinic anhydride derivatives, polyvinylpyrrolidones, perfluoroalkyl acids derivatives, mixtures thereof and mixtures with diluents. Another aspect of the present invention is a process for the preparation of such a SC which comprises
  - air-milling of 50 to 400 g/L of one or more crop protection active compounds (a) optionally in the presence of one or more anionic dispersants (c2), and/or a milling aid such as kaolin or silica, and
    - (2) mixing all the components (a) to (g) in a dissolver.

[0006] Furthermore, the invention relates to a method for the control of pests at a locus which comprises diluting a SC according to the invention with water and treating the said locus with the obtained diluted formulation.

[0007] Those and other objects and features of the invention will become more apparent from the detailed description set forth hereinbelow.

# DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0008] It has now been found that, surprisingly, stable aqueous SC formulation comprising one or more crop protection active compounds (a) and one or more adjuvants (b) in combination with one or more non-ionic dispersants (c1) and/or one or more anionic dispersants (c2) and can be prepared.

[0009] The biological activity of the active ingredients (a) can be increased by including the adjuvants (b) in the spray dilution or directly in the formulation. However, according to the present invention the adjuvants (b) are incorporated into the concentrated formulation.

[0010] The term pests as used hereinabove and hereinbelow includes but is not limited to plant pathogens, insects and weeds.

[0011] In principle all crop protection active compounds can be used for the non-aqueous concentrated suspensions according to the invention. However, solid crop protection active compounds are preferred.

[0012] As a rule solid crop protection active compounds are used which have a low solubility in water. A solubility of less than 10 g/L, in particular less than 5 g/L in water is preferred.

10 [0013] The compositions of this invention can be applied to the plants or their environment with other active substances. These active substances (a) can be either fertilizers or agents which donate trace elements or other preparations which influence plant growth. However, they can also be selective herbicides, insecticides, functions, bactericides, nematicides, algicides, molluscicides, ordenticides, wincides, compounds inducing resistance into plants, biological control agents such as viruses, bacteria, redenticides, fungi and other microorganisms, repellents of birds and animals, and plant growth regulators, or mixtures of several of these preparations.

[0014] The active ingredients, which are provided in the form of the aqueous SC formulation according to the invention, include all suitable biologically active compounds for plant protection, preferably fungicides, herbicides, insecticides, acaricides, nematicides and repellents, in particular fungicides. Active ingredients which are solid at room temperature are preferred, in particular those with a melting point of higher than 50 °C.

(2015) Mixtures of different biologically active compounds can have a broader spectrum of activity than a single compound atone. Furthermore, these can exhibit a synergistic effect compared with the single active ling eddents. In a preferred embodiment, the formulation of the present invention can be used with a mixture of active ingredients in the case of mixtures one of the active ingredients can be dissolved in the continuous phase of the SC formulation according to the invention.

25 [0016] Preferred fungicides for use in the compositions of the present invention are the commercially available compounds selected from the group consisting of:

AC 382042, anilazine, azoxystrobin, benalaxyl, benomyl, binapacryl, bitertanol, blasticidin S, Bordeaux mixture, bromuconazole, bupirimate, captafol, captan, carbendazim, carboxin, carpropamid, chlorbenzthiazon, chlorothalonil, chlozolinate, copper-containing compounds such as copper oxychloride, and copper sulfate, cycloheximide, 30 cymoxanil, cypofuram, cyproconazole, cyprodinil, dichlofluanid, dichlone, dichloran, diclobutrazol, diclocymet, diclomezine, diethofencarb, difenoconazole, diflumetorim, dimethirimol, dimethomorph, diniconazole, dinocap, ditalimfos, dithianon, dodemorph, dodine, edifenphos, epoxiconazole, etaconazole, ethirimol, etridiazole, famoxadone, fenapanil, fenamidone, fenarimol, fenbuconazole, fenfuram, fenhexamid, fenpiclonil, fenpropidin, fenpropimorph, fentin, fentin acetate, fentin hydroxide, ferimzone, fluazinam, fludioxonil, flumetover, fluquinconazole, flusilazole, flusulfamide, flu-35 tolanii, flutriafoi, folpet, fosetylaluminium, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole, IKF-916, imazalil, iminoctadine, ipconazole, iprodione, isoprothiolane, iprovalicarb, kasugamycin, KH-7281, kitazin P, kresoximmethyl, mancozeb, maneb, mepanipyrim, mepronil, metalaxyl, metconazole, methfuroxam, MON 65500, myclobutanil, neoasozin, nickel dimethyldithiocarbamate, nitrothalisopropyl, nuarimol, ofurace, organo mercury compounds, oxadixyl, oxycarboxin, penconazole, pencycuron, phenazineoxide, phthalide, polyoxin D, polyram, probenazole, prochlo-40 raz, procymidione, propamocarb, propiconazole, propineb, pyrazophos, pyrifenox, pyrimethanil, pyroquilon, pyroxyfur, quinomethionate, quinoxyfen, quintozene, spiroxamine, SSF-126, SSF-129, streptomycin, sulfur, tebuconazole, tecloftalame, tecnazene, tetraconazole, thiabendazole, thifluzamide, thiophanate-methyl, thiram, tolclofosmethyl, tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, tricyclazole, tridemorph, trifloxystrobin, triflumizole, triforine,

triticonazole, validamycin A, vinclozolin, XRD-563, zarilarnid, zineb, ziram.
[0018] In addition, the formulations according to the invention may contain at least one compound of the following classes of biological control agents such as viruses, bacteria, nematodes, tungi, and other microorganisms which are suitable for the control of insects, weeds or plant diseases, or to induce host resistance in the plants. Examples of such biological control agents are: Bacillus thuringiensis, verticillium lecanii, Autographica adifornica MPV, Beauvaria bassiana, Ampelomyces quiscoulis, Bacilis subtlis, Pseudomonas fluorescens, Steptomyces griscovinidis and Tichodorii.

50 harzianum.

[0019] Moreover, the formulations according to the invention may contain at least one chemical agent that induces the systemic acquired resistance in plants such as, for example, isonicotinic acid or derivatives thereof, 2,2-dichloro-3.3-dimethylcopropylcarboxic acid or BION.

[0020] Also preferred compositions can include derivatives of benzoylbenzenes which are disclosed, for example, by European Patent Applications EP 0 727 141, in particular the compounds of formula I

$$(R^{2})_{m}$$
 $R^{1}$ 
 $Q$ 
 $R^{4}$ 
 $(R^{7})_{n}$ 
 $R^{5}$ 
 $(I)$ 

wherein

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R1 represents a halogen atom, an optionally substituted alkyl, alkanoyloxy or alkoxy group; or a hydroxy group,

R2 represents a halogen atom, an optionally substituted alkyl group,

R3 represents a halogen atom or an optionally substituted alkyl group,

m is 0 or an integer of 1 to 3:

R4 independently represents a halogen atom, an optionally substituted alkyl or alkoxy group or a nitro group;

R<sup>5</sup> represents an optionally substituted alkyl group;

R<sup>6</sup> represents a halogen atom, a cyano, carboxy, hydroxy or nitro group or an optionally substituted alkyl, alkoxy, alkenyl, alkylthio, alkylsulphinyl, alkylsulphonyl or amino group;

R<sup>7</sup> represents a halogen atom or a nitro group, an optionally substituted alkyl, alkoxy, alkenyloxy, alkynyloxy, alkythio, cycloalkyl, cy

n is 0. 1 or 2.

[0021] Preferred are those compounds of formula I wherein  $\mathbb{R}^1$  represents a, chlorine atom or a methyl, methoxy or a hydroxy group and  $\mathbb{R}^7$  represents a chlorine atom or a methyl group;  $\mathbb{R}^3$  represents a hatogen atom;  $\mathbb{R}^4$  and  $\mathbb{R}^5$  each represents a methyl group; and  $\mathbb{R}^5$  and  $\mathbb{R}^7$  each represent a  $\mathbb{C}_{1-6}$  alkoxy or a benzyloxy group; m is 0 or 1 and n is 1. [0022] Particularly preferred are those compounds of formula I wherein

R1 represents a methoxy group; most preferred are the following benzoylbenzenes:

6-butasy-2,8-dichlaro-4',5-dimethoxy-2-methybenzophenone (coded BB-1); 2,6-dichlaro-4',5-dimethoxy-6'-(2fluorobenzylaxy)-2-methylbenzophenone (coded BB-2); 6-benzylasy-4',5-dimethoxy-2,6-dimethyl-2-methybenzophenone (coded BB-3); and 3-bromo-2',6-dimethyl-2',4',5',6'-teramethoxybenzophenone (coded BB-4).

[0023] Preferred herbicides are the commercially available compounds selected from the group consisting of:

2.4-D. 2.4-D.B. 2.4-D.B. acetochlor, acifluorfen, alachlor, allovydim, ametydione, amidosalfuron, asulam, atrazin, azimsulfuron, bertfureste, bensulfuron, bentacon, bienox, brombattide, bromovnjil busachlor, calenstrole, carefertizacone, chloridazon, chloridazon, chloriduron, c

[0024] Furthermore preferred are the derivatives of anyloxypicolineamides which are disclosed, for example, by European Patent Application EP-A0 447 004, in particular, N-(4-fluorophenyl) 6-(3-trifluoromethylphenoxy)-pyrid-2ylcarboxamide having the proposed common name picolinaten.

[0025] Examples of insecticidal compounds are alpha-cypermethrin, benfuracarb, BPMC, buprofezine, carbosulfan, cartap, chlorfenviriphos, chlorpyriflos-methyl, cycloprothrin, cypermethrin, estenvalerate, ethofengrox, fengropathrin, flucythrinate, flufenoxuron, hydramethylnon, imidacloprid, isoxathion, MEP, MPP, nitenpyram, PAP, permethrin, propaphos, pymetrozine, silafluofen, tebufenozide, teffubenzuron, temephos, terbufuos, tetrachlorviriphos and friazamate.

[0026] Liquid active ingredients such as for example fenpropimorph can be formulated according to the present invention by adsorbing the active ingredient onto a carrier.

[0027] As a rule the non-aqueous SC according to the invention comprises by 50 to 400 g/L, preferably 75 to 375 g/L, in particular 80 to 350 g/L of one or more crop protection active compounds.

- [0028] The adjuvants (b) are preferably selected from the group consisting of amine alkoxylates, alkylpolyglycosides, alkenyl succinic acid derivatives, polyvnylpyrolidones, perfluoroalkyl acid derivatives, in particular perfluoro $(C_{6-13})$  alkylphosphoric acids, perfluoro $(C_{6-13})$  alkylphosphoric acids, perfluoro acids, perfluoro with diluents.
- 10 [0029] The aliphatic moieties of the amines ethoxylates may be straight-chained or branched. Preferably these compounds correspond to a digomer of the following formula

15 in which

n is an integer from 9 to 20, in particular 12 to 18; x is an integer from 2 to 14, in particular 2 to 10.

20 [0030] Of particular interest are those polyalkoxylated aliphatic amines, which are liquids at temperatures down to at least 20°C having a viscosity of 100 to 1000 mPa \* s at 25°C. The compounds which are commercially available under the trademark Bero<sup>®</sup> (Akzo-Nobel), in particular Bero<sup>®</sup> 331 has been proven to be especially advantageous. [0031] The alklypolyglycosides (APG) are obtainable from a acti-datalyzed Fischer reaction of starch or glucose syrups with fatty alcohols, in particular C<sub>8-18</sub> alcohols. Most preferred are C<sub>8-10</sub> and C<sub>12-14</sub> alklypolyglycosides (APG) are commercially available for example under the tradenames Agrimul<sup>®</sup> and Glucopon<sup>®</sup> which are APGs diuted with water, in particular Glucopon<sup>®</sup> 215CSUP or Glucopon<sup>®</sup> 600CSUP front Henkel KGaA or Abus<sup>®</sup> 430, Abus<sup>®</sup> 458, Abus<sup>®</sup> 458.

[0032] Preferred polyoxyalitylene triglycericles are as a rule obtainable by alloxylation of triglycerides. The alloxylation of triglycerides results in mixtures of compounds with none to three glyceride side chains having 9 - 24, prefetably
12 - 22 and in particular 14 - 20 C-atoms, in particular with ethyleneoxide. The allphatic moleties of the said triglycerides
may be straight-chained or branched. Prefetably these compounds correspond to mixed oligomers resulting from the
alloxylation of castor or cando call. Most preferred are castor and cando all eithoryside having 20 to 50, in particular
35 RT40.

8 RT40.

[0033] Preferred alkenyl succinic acid derivatives are compounds of formula

are APGs diluted with hydrotrope agents, from Uniqema (formerly ICI Surfactants).

$$X-(P^1)_x-R$$
 $X-(P^2)_y-R$ 

or salts thereof, in which

R represents a C<sub>4-18</sub> alkyl group, in particular a hexyl, heptyl or dodecyl group;

X represents O or N(C<sub>1-6</sub> alkyl);

P<sup>1</sup> and P<sup>2</sup> each represent a polymer back bone selected from the formulae (1) and(2):

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$$-CH_{\overline{z}}CH_{\overline{z}}-O-HOOHOOH$$
(1)
(2)

R' represents a hydrogen atom or an alkyl group, x represents 0 or an integer from 1 to 10, and y represents an integer from 1 to 10.

Preferred are alkenyl succinic acid diglucamides, alkenyl succinic acid alkoxylates and alkenyl succinic acid alkylpolyglykosides (WO 96/20203), in particular Atplus® ADG 1001 and Atplus® ADG 1201 obtainable from Uniqema. Preferred polyvinylpyrrolidones (PVP) have an average molecular weight of more than 6000 g/mol, in particular 7000 to 9000 α/mol, most preferred is a PVP having an average molecular weight of 8000 α/mol which is available as Agrimer® 15 from ISP.

As a rule the aqueous SC according to the invention comprises 50 to 500 g/L, preferably 75 to 450 g/L, in particular 150 to 400 g/L of one or more adjuvants (b).

The non-ionic dispersants (c1) are preferably liquid polyalkoxylated alighatic fatty acids or straight-chained alcohols. These adjuvants are as a rule obtainable by alkoxylation of fatty acids or straight-chained alcohols having 9 -24, preferably 12 - 22 and in particular 14 - 20 C-atoms, with alkyleneoxide having 2 - 6, preferably 2 - 3 C-atoms, in particular with a mixture of ethylenoxide and propyleneoxide. Preferably these compounds correspond to mixed random or block oligomers of the following formula

in which

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r is 0 or 1, and the average of the indexes given is as follows:

n is an integer from 9 to 20, in particular 15 to 19; x is an integer from 4 to 22, in particular 5 to 18; and

v is an integer from 6 to 12, in particular 7 to 10.

Of particular interest are those polyalkoxylated alighatic alcohols, which are liquids at temperatures down to 40 [0038] at least 20°C having a viscosity of 30 to 100, in particular 50 to 80 mPa • s at 25 °C. The compounds which are commercially available under the trademark Synperonic® (Uniqema), in particular Synperonic® 91-6.

In preferred embodiment of the present invention the non-ionic dispersant (c1) is a fatty acid or phenol. These dispersants are as a rule obtainable by alkoxylation fatty acids or phenols.

Preferred dipersants (c1) are for example Arkopal<sup>®</sup>-type alkylarylethoxylates (Clariant GmbH former Hoechst AG) or Genapol®-type (Clariant GmbH former Hoechst AG) alkanoylethoxylates. Another preferred dispersant (c1) is a nonviphenolethoxylate for example Symperonic® NP-4, which is com-[0041]

mercially available from Unigema.

[0042] Furthermore preferred dispersants (c1) are are polyethyleneoxide-polypropyleneoxide block-copolymers of formula

#### HO-(CH2CH2O),(C2H2(CH2)O),-(CH2CH2O),H,

in which

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the sum of x and z is an integer from 1 to 80, in particular 2 to 75; and v is an integer from 10 to 70, in particular 20 to 60.

[0043] Most preferred are the Pluronic<sup>®</sup>-type block-copolymers, which are available from BASF AG, in particular Pluronic<sup>®</sup> PE 10500.

[0044] As a rule the aqueous SC according to the invention comprises 5 to 75 g/L, preferably 7.5 to 40 g/L, in particular 8 to 30 g/L of one or more non-ionic dispersants (c1).

5 (0045) The anionic dispersant (£2) is as a rule an alkeli or earth alkeli sulfonate, which includes also concentrated mixtures of such an alkeli or earth alkeli sulfonate with a polar ditunet such as an alcohol an arromatic hydrocathon, representably butanol, 2-ethylhexanol or Solvesso® 200. Such a mixture preferably consists of 40 to 90 wt. % of at least one alkeli or earth alkeli sulfonate and 10 to 60 wt. % of an organic dituent. Ammonium, alkeli and earth alkeli alkylbracere sulfonates such as Phodocal® 70/16 (Phodia, formetry 10 Phohe-Poulenc) or Phenylsulfonat CA.100 (Clariant GmibH, formetry Hoechst AG) or isoproplammonium dodecy benzene sulfonates such as software 30/16 (Phodia, formetry 10 Phohe-Poulenc) or Phenylsulfonat CA.100 (Clariant GmibH, formetry Hoechst AG) or isoproplammonium dodecy benzene sulfonate such as Afox® 3008 (Uniquena). In particularly preferred embodiment of this invention the anionic dispersant is an alkylnaphthalene sulfonic acid formaldehyde condensate such as Morwet® D425 (Witco Corporation, USA).

[0046] As a rule the aqueous SC according to the invention comprises 10 to 100 g/L, preferably 10 to 80 g/L, in particular 15 to 75 g/L, of one or more anionic dispersants.

[0047] The appropriate relative amounts of active ingredient (a) and the adjuvant (b) lie, in accordance with the invention, between 1.0.5 and 1:100, preferably between 1.0.5 and 1:100 and, in particular, between 1.1 and 1.5. In general and within certain limits, the pesticidal efficacy can be enhanced to a higher degree by the addition of larger amounts of the adjuvant (b) as is shown in the experimental results described below.

0 [0048] Recommended doses for various applications are known for the crop protection active compounds (a) where the efficacy can be enhanced in accordance with the invention. Addition of the adjuvants suggested here can (depending on the active ingredient, the adjuvant and their amounts) reduce the amount of active ingredient per hectare required in these recommendations by half or more, whereby it becomes possible to control additional diseases at reasonable doses.

25 [0049] An important advantage is the rapid onset and the high persistency of activity on use of the new additives. This enlarges the period for application of the pesticide and makes its use more flexible.

[0050] The pesticidal formulations according to the present invention can be used protectively and curatively.

[0051] As a rule the aqueous SC according to the invention comprises 200 to 800 g/L, preferably 300 to 700 g/L, in particular 350 to 650 g/L of water.

30 [0052] In a particularly preferred embodiment according to this invention the non-aqueous SC essentially consists of

- (a) 75 to 350 g/L, preferably 100 to 300 g/L of one or more crop protection active compounds, in particular a compound of formula I;
- (b) 75 to 450 g/L, preferably 100 to 300 g/L of one or more adjuvants selected from the group consisting of alkoxy-lated amines, alkypolyglycosides and alkenyl succinic anhydride diglucamides.
  (c) at least one surfactant selected from the groups (c1) and (c2):
  - (c1) 5 to 25 g/L, preferably 7.5 to 20 g/L of one or more non-ionic dispersant;
  - (c2) 10 to 50 g/L, preferably 15 to 40 g/L of one or more anionic dispersant;
    - (d) 0 to 75 g/L, preferably 0.5 to 60 g/L of an anti-freezing agent;
  - (e) 0 to 5 g/L, preferably 0.5 to 5 g/L of a defoamer;
- (f) up to 10 g/L, preferably 0.5 to 5 g/L of one or more preservatives,
- (g) 300 to 700 g/L water, and

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(h) up to 30 g/L, preferably 0.5 to 15 g/L of one or more structure agents, preferably Xanthan gum such as Rhodopol® 23 from Rhodia and/or hydrated silicates such as Attagel® 50 from Engelhard Corp. or Veegum® T from Vandrebill Export Corp.

50 (0053) The adjuvants (b) according to the invention, the pesticidal active compounds (a) and dispersants (c) and water and optionally one or more anti-freezing agents (d) and/or defoamers are processed to suspension concentrates according to the invention by well-established procedures. These procedures include intensive mixing and/or milling of the active ingredients with the other substances, such as solvents, wetting agents, and adjuvants. The form of application such as spraying, atomizing, dispersing or pouring may be chosen like the compositions according to the desired objectives and the given circumstances.

[0054] Suspension concentrates according to the present invention are usually produced so as to obtain a stable, non-sedimenting flowable product and usually contain 5 to 40% w/v active ingredient; 5 to 50% w/v adjuvant, 0.5 to 17.5% w/v of dispersing agents, 0 to 15% w/v antifreezing agent, 0 to 10% w/v of suspending agents such as protective

colloids and thixotropic agents, 0 to 2.5% w/v preservatives, 0 to 10% w/v of other additives such as defoamers, corrosion inhibitors, stabilizers, penetrants and stickers, and an organic liquid in which the active ingredient is substantially insoluble.

[0055] Preferred anti-loam agents (e) are silica, polydialkylsiloxanes and mixtures thereof, in particular Rhodorsil®
416, Rhodorsil® 426R or Rhodosil® 434 from Rhodosil. Particularly preferred is a combination of polydimethylsiloxanes
and perfluoroalkylphosphonic / perfluoroalkylphosphina caids.

[0056] The term preservatives (f) includes chemical stabilizers to prevent decomposition of the compound of formula I during storage such as alkaline earth and transition metal sulfates and biocides, in particular bactericides such as Proxel® CXL (Zeneca)

10 [0057] In a preferred embodiment the crop protection compound (a) is air-milled optionally in the presence of dispersant (c2) before admixing the components (b) to (q) and optionally (h).

[0058] The finished non-aqueous suspension concentrates according to the invention are stable in storage, i.e. even on storage over a relatively long period. Although phase separation may occur upon storage due to sedimentation of the active ingredient, no aggregates are formed. The SCs according to the present invention allow the inclusion of 15 high loadings of one or more adjuvants in a one-pack formulation with a pessibide and, therefore, offer the advantage of

nign loatings or one or more adjuvants in a one-pack formulation with a pessicide and, meretore, oner the advantage or an optimized and easy-to-use formulation of the crop protection active compound. The separate addition of an adjuvant by the end-user before application has therefore become unnecessary.

[0059] Aqueous dispersions and emulsions, for example compositions obtained by diluting the formulated product according to the invention with water, also lie within the scope of the invention.

80 [0060] As a commodify the compositions may preferably be in a concentrated form whereas the end user generally employs diluted compositions. The compositions may be diluted to a concentration down to 0.001% of active ingredient. The doses are usually in the range of 0.01 to 10 kg a.i./ha.

[0061] For a more clear understanding of the invention, specific examples are set forth below. These examples are merely illustrations and are not to be understood as limiting the scope and underlying principles of the invention in any 25 way. Various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the following examples and foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

[0062] Examples of aqueous suspension concentrates according to the invention are shown in the following examples A to M:

### Identity of Ingredients used in Examples

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Name	Function	Identity
Agrimer 15 (ISP)	Adjuvant	Polyvinylpyrrolidone having a molecular
		weight of 8,000 g/mol
Agrimer 30 (ISP)	Adjuvant	Polyvinylpyrrolidone having a molecular
		weight of 38,000 g/mol

	Name	Function	Identity
_	Agrimer VA7W (ISP)	Adjuvant	Polyvinylacetate polyvinylpyrrolidone
5			copolymer
	Agsol EX 8 (ISP)	Adjuvant	N-octylpyrrolidone
	Arkopal N-80 (Clariant)	Adjuvant	Nonylphenol polyglycolether (8 EO)
10	Atplus 450® (Uniqema)	Adjuvant	Alkylpolysaccharide blend
	Atplus 469® (Uniqema)	Adjuvant	Alkylpolysacchande blend -
	Atplus 430® (Uniqema)	Adjuvant	Alkylpolysaccharide blend
15	Atplus 435® (Uniqema)	Adjuvant	Alkylpolysaccharide blend
	Atplus MBA 11-7®	Adjuvant	branched alcohol ethoxylate
	(Unigema)		
20	Berol 381 (Akzo-Nobel)	Adjuvant	Amine ethoxylate
	Bevaloid 6338 (Rhodia)	Defoamer	Emulsion of inert polymeric substances
	Eumulgin RT40 (Henkel)	Adjuvant	Castor oil ethoxylate (40 EO)
25	Fluorad FC-430 (3M)	Adjuvant	Perfluoroaliphatic polymeric ester
	Fluorad FC-129 (3M)	Adjuvant	Perfluoroalkylsulfonate
	Fluowet PL80 (Clariant)	Adjuvant	80 % mixture of perfluorinated
30			alkylphosphinic / alkylphosphonic acids
	Geropon T36 (Rhodia)	Dispersant	Sodium polycarboxylate
	Glucopon 600CSUP	Adjuvant	C <sub>12.14</sub> alkylpolyglycoside in water
35	(Henkel)		
	Glucopon 215CSUP	Adjuvant	C <sub>8-10</sub> alkylpolyglycoside in water
	(Henkel)		
40	Laponite RDS (Solvay	Structure agent	Sodium Magnesium Silicate and
***	Alkali GmbH)		Tetrasodium Phosphate
	Morwet D425 (Witco)	Dispersant	Alkylnaphthalene sulfonic acid
			formaldehyde condensate
45	Pluronic PE10500 (BASF)	Dispersant	Ethyleneoxide/propyleneoxide block
			copolymer
	Proxel GXL (Zeneca)	Biocide	aqueous dipropylene glycol solution
50			containing 20 % 1,2-benzisothiazoli-3-
			one

Name	Function	Identity
Rhodopol 23 (Rhodia)	Structure agent	heteropolyscchande having a molecular
		weight of about 2,000,000 g/mol
Atplus ADG 1001	Adjuvant	C <sub>12</sub> alkenyl succinic anhydnde
(Uniqema)	1	diglucamide
Atplus ADG 1201	Adjuvant	50 % C <sub>12</sub> alkenyl succinic anhydride
(Uniqema)		diglucamide in propylene glycol
SAG 220 (Witco	Defoamer	Polydimethylsiloxane emulsion
Surfactants)		
Silicon Antifoam TP 20	Defoamer	Polydimethylsiloxane emulsion
(OSi Specialities GmbH)		
Silica FK 320 (Degussa	Defoamer	Amorphous silica
AG)		
Rhodorsil 426 R (Rhodia)	Defoamer	polydimethylsiloxane emulsion
Soprophor FL (Rhodia)	Dispersant	Ammonium polyarylphenyl ether
		phosphate
Supragil MNS/90 (Rhodia)	Dispersant	Sodium naphthalene sulfonate
		formaldehyde condensate
Vanisperse CB (Lignotech,	Dispersant	Sodium ligninsulfonate
Norway)		
Veegum T (Vanderbiit Exp.	Structure agent	Hydrated magnesium aluminium silicat
Corp., USA)	ļ	
Veegum Pro (Vanderbilt	Structure agent	Trimethamine magnesium aluminium
Exp. Corp., USA)		silicate
Synperonic 91-6	Adjuvant	alcohol ethoxylate
(Uniqema)		

### Examples 1 to 3

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[0063] The following SC formulations according to the invention are prepared by mixing the ingredients with the exception of the structure agent, the antifreeze agent and the adjuvant in a dissolver. Subsequently, the suspension is milled using a Dyno-mill. The adjuvant is then stirred into the milled suspension. Subsequently, a suspension of the structure agent and the antifreeze agent is produced and also stirred into the milled suspension.

55 [0064] Alternatively, the structure agent can be added to the un-milled suspension and milled together with the active ingredient.

[0065] The obtained SC formulations are compared with similar SC formulations (C-1 and C-2), in which the adjuvant (b) was replaced by n-octylpyrrolidone or an alcohol ethoxylate (Synperonic 91-6)

#### [0066] The following formulations are obtained:

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		Conc	entration	(g/L)	
			Example		
Ingredient	1	2	3	C-1	C-2
BB-4	200	200	200	200	200
Morwet D425	20	20	20	20	20
Pluronic PE 10500	10	10	10	10	10
Proxel GXL	2	2	2	2	2
Rhodorsil 426R	2	2	2	2	2
Rhodopol 23	3	3	3	3	3
Propylene glycol	50	50	50	50	50
Agsol Ex8			.	50	
Synperonic 91-6	-	-	-	200	250
Atplus 450	250	-	-	-	
Atplus 469		250	.	-	
Atplus ADG 1201	-	-	250	-	-
Water	to 1L	to 1L	to 1L	to 1L	to 1L

[0067] The density, and the particle size distribution upon storage for two weeks at room temperature (RT), at 40  $^{\circ}$ C (2W40  $^{\circ}$ C) and at 54  $^{\circ}$ C (2W54  $^{\circ}$ C) of the SC formulations are shown in the following table I:

				Example				
Properties		1	2	3	C-1	C-2		
Density	[g/mL]	1.106	1.121	1.116	1.078	1.085		
Particle size	x <sub>10</sub> [μm]	0.74	0.74	0.76	0.88	0.74		
distribution	x <sub>50</sub> [μm]	1.92	1.92	1.98	3.19	1.95		
(RT)	x <sub>90</sub> [μm]	4.83	4.78	5.00	6.77	4.77		
Particle size	x <sub>10</sub> [μm]	0.73	0.74	0.73	1.04	0.82		
distribution	x <sub>50</sub> [μm]	1.87	1.88	1.89	3.73	2.28		
(2W40 °C)	x <sub>90</sub> [μm]	4.56	4.50	4.70	7.59	5.44		
Particle size	x <sub>10</sub> [μm]	0.74	0.76	0.74	1.39	1.00		
distribution	x <sub>50</sub> [μm]	1.90	1.96	1.88	5.07	2.89		
(2W54 °C)	x <sub>90</sub> [μm]	4.51	4.42	4.49	10.16	6.54		

[0068] Whereas the particle size distribution of the formulations according to the present invention is constant upon storage at elevated temperature, the particle size increases drastically with alcohol ethoxylates as adjuvants alone or with an N-allylpyrroidonu.

#### Examples 4 to 6

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[0069] The following SC formulations according to the invention are prepared analogously to examples 1 to 3.

[0070] The following formulations are obtained:

Concentration (g/L) Example Ingredient BB-4 200 200 200 Morwet D425 20 20 20 Pluronic PE 10500 10 10 10 Proxel GXL 2 2 2 Rhodorsil 426R 2 2 Rhodopol 23 3 3 Propylene glycol 50 50 50 Agrimer 15 250 Fluowet PL80 70 Atplus 430 250 Water to 1L to 1L to 1L

[0071] The density, and the particle size distribution upon storage for two weeks at room temperature (RT), at 40 °C (2W40 °C) and at 54 °C (2W54 °C) of the SC formulations are shown in the following table II:

Table II

			Example	
Properties		4	5	6
Density	[g/mL]	1.141	1.100	1.121
Particle size	x <sub>10</sub> [μm]	0.75	0.76	0.75
distribution	x <sub>50</sub> [μm]	1.98	2.04	1.95
(RT)	х <sub>90</sub> [µm]	4.98	5.39	4.02
Particle size	х <sub>10</sub> [µm]	0.73	0.76	0.74
distribution	x <sub>50</sub> [μm]	1.86	2.03	1.90
(2W40 °C)	х <sub>90</sub> [µm]	4.55	5.26	4.09
Particle size	х <sub>10</sub> [µm]	0.75	0.75	0.75
distribution	x <sub>50</sub> [μm]	1.92	2.03	1.95
(2W54 °C)	x <sub>90</sub> [μm]	4.55	5.38	4.01

[0072] The particle size distribution of the formulations according to the present invention is constant upon storage at elevated temperature.

#### Example 7

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[0073] The following SC formulation according to the invention is prepared analogously to Examples 1 to 3. It is compared with a similar SC formulation (C-3), in which the adjuvant (b) was replaced by a polyoxyethylene sorbitol ester (Tween 80).

[0074] The following formulations are obtained:

	Concentration (g/L)			
	Exa	mple		
Ingredient	7	C-3		
BB-4	200	200		
Morwet D425	20	20		
Pluronic PE 10500	10	10		
Proxel GXL	2	2		
Rhodorsil 426R	2	2		
Rhodopol 23	3	3		
Propylene glycol	50	50		
Atplus 435	250	-		
Tween 80	- 1	250		
Water	to 1L	to 1L		

30 [0075] The density, and the particle size distribution upon storage at room for two weeks at temperature (RT), 2 at 40 °C (2W40 °C) and at 54 °C (2W54 °C) of the SC formulations are shown in the following table III:

	Example		
Properties		7	C-3
Density	[g/mL]	1.111	1.108
Particle size	x <sub>10</sub> [μ <b>m</b> ]	0.75	0.75
distribution	x <sub>50</sub> [μm]	1.97	2.27
(RT)	x <sub>90</sub> [μ <b>m</b> ]	4.97	4.64
Particle size	x <sub>10</sub> [μ <b>m</b> ]	0.74	0.84
distribution	x <sub>50</sub> [μm]	1.89	2.27
(2W40 °C)	х <sub>90</sub> [µm]	4.54	5.40
Particle size	х <sub>10</sub> [µm]	0.76	0.98
distribution	х <sub>50</sub> [µ <b>m</b> ]	1.96	2.74
(2W54 °C)	х <sub>90</sub> [µm]	4.64	6.26

[0076] Whereas the particle size distribution of the formulations according to the present invention is constant upon storage at elevated temperature, the particle size increases drastically with polyoxyethylene sorbitol esters as adjuvants.

#### Examples 8 to 12

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[0077] The following SC tormulations according to the invention are prepared analogously to Examples 1 to 3. [0078] The following formulations are obtained:

		Concentration (g/L)					
			Example	,			
Ingredient	8	9	10	11	12		
BB-4	200	200	200	200	200		
Morwet D425	20	20	20	20	20		
Pluronic PE 10500	10	10	10	10	10		
Proxel GXL	2	2	2	2	2		
Rhodorsil 426R	2	2	2	2	2		
Rhodopol 23	3	3	3	3	3		
Propylene glycol	50	50	50	50	50		
Berol 381	250	-		-	-		
Fluorad FC430		100	-	-	-		
Fluorad FC129		-	100	-	-		
Glucopon 600 CSUP		-		250	-		
Glucopon 215 CSUP	-	-	-	-	250		
Water	to 1L	to 1L	to 1L	to 1L	to 1L		

[0079] The density, and the particle size distribution upon storage for two weeks at room temperature (RT) and at 54 °C (2W54 °C) of the SC formulations are shown in the following table IV:

Table IV

		Example				
Properties	8	9	10	11	12	
Density	[g/mL]	1.101	1.105	1.101	1.103	1.085
Particle size	x <sub>10</sub> [μm]	0.72	0.74	0.73	0.73	0.74
distribution	x <sub>50</sub> [μm]	1.97	1.96	1.96	2.05	2.05
(RT)	х <sub>90</sub> [µm]	5.35	5.50	5.52	5.85	5.78
Particle size	x <sub>10</sub> [μm]	0.70	0.70	0.71	0.72	0.72
distribution	x <sub>50</sub> [μm]	1.87	1.84	1.84	1.96	1.92
(2W54 °C)	x <sub>90</sub> [μm]	5.12	5.01	5.00	5.57	5.30

[0080] The particle size distribution of the formulations according to the present invention is constant upon storage at elevated temperature.

# Examples 13 to 15

[0081] The following SC tormulations according to the invention are prepared analogously to Examples 1 to 3

#### [0082] The following formulations are obtained:

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	Concentration (g/L)				
		Example			
Ingredient	13	14	15		
BB-4	200	200	200		
Morwet D425	20	20	20		
Pluronic PE 10500	10	10	10		
Proxel GXL	2	2	2		
Rhodorsil 426R	2	2	2		
Rhodopol 23	3	3	3		
Propylene glycol	50	50	50		
SCS 3631	250	-			
Emulgin RT40		250			
Agrimer 30	-		100		
Water	to 1L	to 1L	to 1L		

[0083] The density, and the particle size distribution upon storage for two weeks at room temperature (RT) and 2 weeks at 54 °C (2W54 °C) of the SC formulations are shown in the following table V:

Гa		

			Example	
Properties		13	14	15
Density	[g/mL]	1.126	1.107	1.104
Particle size	x <sub>10</sub> [μm]	0.72	0.72	0.73
distribution	x <sub>50</sub> [μm]	2.03	1.95	2.98
(RT)	x <sub>90</sub> [μm]	5.77	5.44	5.50
Particle size	x <sub>10</sub> [μm]	0.70	0.71	0.70
distribution	x <sub>50</sub> [μm]	1.88	1.91	1.84
(2W54 °C)	х <sub>90</sub> [µm]	5.14	5.45	4.96

[0084] The particle size distribution of the formulations according to the present invention is constant upon storage at elevated temperature.

# 50 Examples 16 to 18

[0085] The following SC formulations according to the invention are prepared analogously to Examples 1 to 3.

	Concentration (g/L)				
Ingredient	Example 16	Example 17	Example 18		
Dimethomorph	375	375	250		
Soprophor FL	15.6	15.6	7.8		
Bevaloid 6338	1.9	1.9	1.3		
Proxel GXL	0.9	0.9	0.7		
Propylene glycol	50	50	33		
Rhodopol 23	1.7	1.7	1.1		
Fluowet PL80	250	-	-		
Atplus 469		250	-		
Glucopon 215 CSUP			500		
Water	to 1 liter	to 1 liter	to 1 liter		
Density (g/mL)	1.16	1.15	1.12		

# Examples 19 to 21

[0086] The following SC formulations according to the invention are prepared analogously to Examples 1 to 3.

	Concentration (g/L)				
Ingredient	Example 19	Example 20	Example 21		
Metconazole	100	100	100		
Vanisperse CB	13.3	13.3	13.3		
Rhodorsil 426R	0.6	0.6	0.6		
Proxel GXL	0.8	0.8	0.8		
Propylene glycol	64	64	64		
Rhodopol 23	1.4	1.4	1.4		
SCS 3631	100		-		
Atplus 469		100	-		
Glucopon 215 CSUP	-		100		
Water	to 1 liter	to 1 liter	to 1 liter		
Density (g/mL)	1.11	1.09	1.08		

# 50 Examples 22 to 24

[0087] The following SC formulations according to the invention are prepared analogously to Examples 1 to 3.

Concentration (q/L) Ingredient Example 22 Example 23 Example 24 Picolinafen 125 150 125 Supragil MNS/90 7.5 9 7.5 7.5 Geropon T36 6.3 6.3 Rhodorsil 426R 0.5 0.6 0.5 Proxel GXL 0.3 0.3 0.3 Citric Acid 3.0 3.6 3.0 Propviene alvool 25 30 25 Rhodopol 23 1.25 1.5 1.25 Agrimer VA7W 500 Atplus 469 400 Glucopon 215 CSUP 500 Water to 1 liter to 1 liter to 1 liter Density (g/mL) 1.10 1.07

#### Example 25

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[0088] The following SC formulation according to the invention is prepared analogously to Examples 1 to 3

Ingredient	Concentration (g/L)
Pendimethalin	300
Agrimer 15	250
Soprophor FL	45
Arkopal N-80	38
Veegum T	4.5
Silicon Antifoam TP 20	5.6
Proxel GXL	0.75
Silica FK 320	3.8
Water	to 1 liter
Density (g/mL)	1.13

[0089] The SCs described in the examples 16 - 25 show insignificant particle growth when stored for 2 weeks at 54°C (2 weeks at 40°C for example 25). When the adjuvant is replaced by the equivalent amount of alcohol ethoxylate (e.g. Symperonic 91-6), unacceptable particle growth is observed in all cases.

# Examples 26 to 28

[0090] The following SC formulations according to the invention are prepared analogously to Examples 1 to 3.

Concentration (a/L) Ingredient Example 26 Example 27 Example 28 BB-4 350 300 300 Morwet D425 30 20 20 Pluronic PE 10500 15 10 10 Atplus 469 437.5 375 375 Rhodorsil 426R 2 SAG 220 5 Proxel GXL 2 2 2 Laponite RDS Rhodopol 23 1 0.35 Veeaum Pro 2.5 Water to 1 liter to 1 liter to 1 liter 1.20 Density (g/mL) 1.16

[0091] The SCs described in the examples 26 - 28 show insignificant particle growth when stored for 2 weeks at 54°C

#### Example 29

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[0092] The following SC formulations according to the invention are prepared analogously to Examples 1 to 3.

Ingredient	Concentration (g/L)
BB-4	300
Morwet D425	75
Pluronic PE 10500	10
Atplus 469	375
SAG 220	10
Proxel GXL	3
Rhodopol 23	0.45
Veegum Pro	2.5
1,2-propylene glycol	50
Water	to 1 liter
Density (g/mL)	1.19

[0093] The SC described in example 29 shows insignificant particle growth when stored for 2 weeks at  $54^{\circ}$ C and 8 weeks at  $40^{\circ}$ C

#### Claims

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- 1. An aqueous, concentrated suspension (SC) for crop protection active compounds which comprises
  - (a) 50 to 400 g/L of at least one crop protection active compound:
  - (b) 50 to 500 g/L of at least one adjuvant, which has the capability of reducing the surface tension in the spray dilution to 40 mN/m or lower and does not promote the particle growth of the crop protection active compound; (c) at least one surfactant selected from the groups (c1) and (c2):
- (c1) 5 to 75 g/L of one or more non-ionic dispersants, and (c2) 10 to 100 g/L of one or more anionic dispersants.
  - (d) up to 150 g/L of one or more anti-freezing agents.
  - (e) up to 25 g/L of one or more defoamers,
    - (f) up to 25 g/L of one or more preservatives, and
      - (g) 200 to 800 g/Lof water,

wherein the adjuvant (b) is selected from the group consisting of amine alkoxylates, polyoxyalkylene triglycerides, alkylpolyglycosides, alkenyl succinic anhydride derivatives, polyvinylpyrrolidones, perfluoroalkyl acids derivatives, and mixtures thereof.

 A SC in accordance with claim 1 wherein the crop protection active compound (a) comprises a benzoylbenzene of formula I

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# 35 wherein

- R<sup>1</sup> represents a halogen atom, an optionally substituted alkyl, alkanoyloxy or alkoxy group; or a hydroxy group,
  R<sup>2</sup> represents a halogen atom, an optionally substituted alkyl group.
- R3 represents a halogen atom or an optionally substituted alkyl group,
- m is 0 or an integer of 1 to 3;
  - R<sup>4</sup> independently represents a halogen atom, an optionally substituted alkyl or alkoxy group or a nitro group; R<sup>5</sup> represents an optionally substituted alkyl group;
  - H° represents an optionally substituted alkyl group;

    R<sup>6</sup> represents a halogen atom, a cyano, carboxy, hydroxy or nitro group or an optionally substituted alkyl,
- alkoxy, alkenyl, alkylthio, alkylsulphinyl, alkylsulphonyl or amino group; R<sup>7</sup> represents a halogen atom or a nitro group, an optionally substituted alkyl, alkoxy, alkenyloxy, alkynyloxy,
  - alkylthio, cycloalkyl, cycloalkyloxy, aryloxy group; and
- n is 0, 1 or 2.
- A SC in accordance with claim 1 comprising 75 to 450 g/L of at least one alkylpolyglycoside, at least one amine ethoxylate or at least one alkenyl succinic anhydride diglucamide.
  - A SC in accordance with claim 1 comprising 55 to 150 g/L of at least one perfluoro(C<sub>6-18</sub>)alkylphosphonic acid, perfluoro(C<sub>6-18</sub>)alkyl-phosphinic acid or a mixture thereof.
- A SC in accordance with claim 1 wherein the ratio of the crop protection active compounds (a) to said adjuvant (b)
  is between 1: 0.5 and 1:100, preferably between 1: 0.75 and 1:10.
  - 6. A SC in accordance with claim 1 comprising in addition to the components (a) to (g): (h) 0.1 to 30 g/l of at least one

thickener.

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- A SC in accordance with claim 1 wherein the non-ionic dispersant (c1) is a block copolymer which consists of a polyoxypropylene and polyoxyethylene moieties.
- A SC in accordance with claim 1 wherein the anionic dispersant (c2) is an amino sulfonate or an alkali or earth alkali sulfonate.
- 9. A method for the enhancement of the efficacy of crop protection active compounds which comprises combining said crop protection active compounds with an effective amount of at least one adjuvant, which has the capability of reducing the surface tension in an aqueous spray dilution to 40 mWm or lower being selected from the group consisting of amine allkoxylates, polyoxyalitylene triglycerides, alkylpolyglycosides, alkenyl succinic anhydride derivatives, polyvinlypyroliones, perfuloroalityl acids derivatives, and mixtures thereof.
- 15 10. A method for combating a fungus at a locus which comprises diluting a formulation as claimed in any of the claims 1 to 8 with water and treating said locus with the obtained diluted aqueous formulation.



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EP 00 30 0669

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